



**AFRL-ML-WP-TP-2007-498**

**A NEW TYPE OF POTASSIUM NIOBATE CRYSTAL:  
UTILIZING THE POTASSIUM SITES (PREPRINT)**

**Dean R. Evans**

**Hardened Materials Branch  
Survivability and Sensor Materials Division**

**JANUARY 2006**

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\*//Signature//

DEAN R. EVANS, Ph.D.  
Agile Filters Project  
Exploratory Development  
Hardened Materials Branch

//Signature//

MARK S. FORTE, Acting Chief  
Hardened Materials Branch  
Survivability and Sensor Materials Division

//Signature//

TIM J. SCHUMACHER, Chief  
Survivability and Sensor Materials Division

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<b>14. ABSTRACT</b> <ul style="list-style-type: none"> <li>• Darker regions (perturbed Fe – FeNb near a AgK) in the crystal exhibit strong contra-directional-TBC.</li> <li>• There is a similar affect for interchanging NiNb for FeNb and RbK for AgK. AuK should work as well, but there's no evidence yet.</li> <li>• The presence of Ag changes the local environment, perturbing the other impurities (i.e. Oh-), and the phonon/Raman modes are strongly affected.</li> </ul> <p style="text-align: right;"><i>Abstract concluded on reverse side</i></p>					
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#### 14. ABSTRACT (concluded)

- Ag was then purposely used as a codopant  $\text{KNbO}_3\text{:Fe}$ , Ag and is responsible for:
  - An enhanced visible/OH- absorption
  - A stronger PV field
  - The strong affect on the Raman scatter
  - A possible increase in trap density (undetermined)
- Codoping with Ag is better than Rb in terms of speed, there's no significant difference in AOD.
- Singly doped Ag and unperturbed Fe are hole conducting, whereas perturbed Fe is electron conducting.

# A New Type of Potassium Niobate Crystal; Utilizing the Potassium Sites



**D. R. Evans J. L. Carns,  
M. A. Saleh, and G. Cook**  
*Air Force Research Laboratory  
Materials and Manufacturing Directorate  
Wright-Patterson Air Force Base, OH*

**S. A. Basun**  
*A. F. Ioffe Physico-Technical Institute  
St. Petersburg, Russia*

**J. M. Seim and G. J. Mizell**  
*VLOC  
New Port Richey, FL*



## Outline



- **Motivation/Background**
- **Modified Material Properties (K-site)**
  - **Enhanced Absorption**
  - **Enhanced Photocurrent**
  - **Enhanced Photorefractive Effect**
  - **Raman Scatter Influence**
- **Summary**



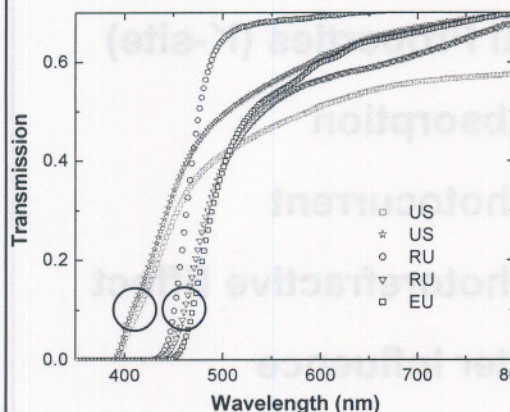
## Motivation



- Some  $\text{KNbO}_3$  crystals, from different growers, have few regions that allow efficient counter-propagating TBC.
- What is the difference between spots that couple and those that don't?
- Can we control the growth process to give homogeneous materials (in terms of TBC)?



## Large Shifts in Band Edges (Dependent of Crystal Origin)



### Three thoughts:

- Different composition (K/Nb)
- Different starting mat'ls
- Post growth issues
- Starting mat'ls are unknown
- Growth procedures unknown
- Poling procedures known for 2 of 3 growers



## Motivation



- Small regions, particularly near the edges, exhibit strong counter-propagating TBC efficiencies.
- We hypothesized that the enhanced TBC was due to contamination from the post-growth poling process (electrodes).
- A series of codoped  $\text{KNbO}_3:\text{Fe},\text{Ag}$  crystals were grown with different concentrations of Ag.

Crystals used  
in this study:

1000 ppm Fe; 1000 ppm Ag

1000 ppm Fe; 5000 ppm Ag

1000 ppm Fe; 10,000 ppm Ag

10,000 ppm Ag

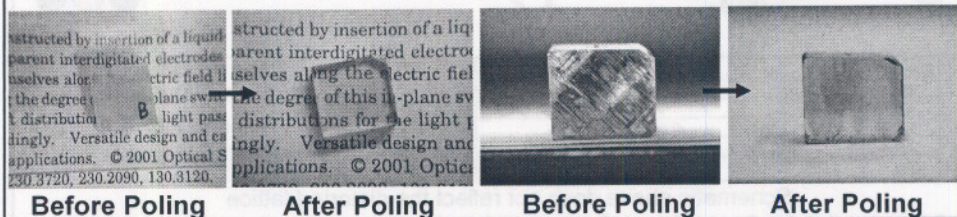


## Domain Poling



- Growth complicated by two solid phase changes:
  - Material starts as cubic
  - Becomes tetragonal at  $435^\circ\text{C}$
  - Orthorhombic below  $225^\circ\text{C}$
- Internal stresses from phase changes create multiple domains and twins
- Poling is required to create a single domain crystal

Without poling, multiple random domains, i.e. sign of the electro-optic coeff. changes throughout the crystal – no/weak coupling

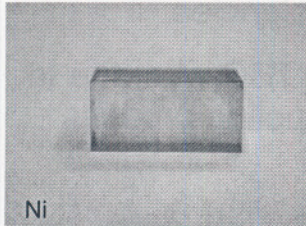




## Unintentional/Intentional Codopants

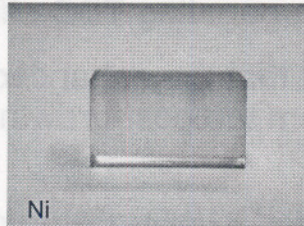


Assumed contamination from diffusion of poling electrodes



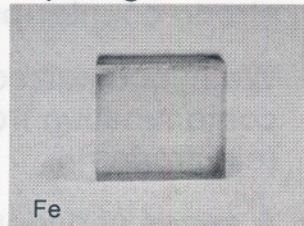
Ni

c-axis



Ni

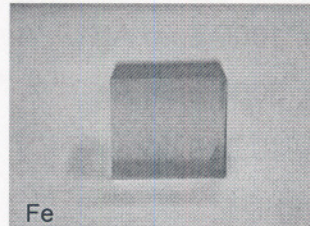
b-axis



Fe

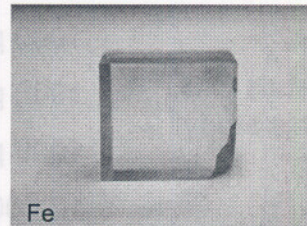
c-axis

Intentionally singly/doubly doped (in the melt) crystals



Fe

No intentional Ag

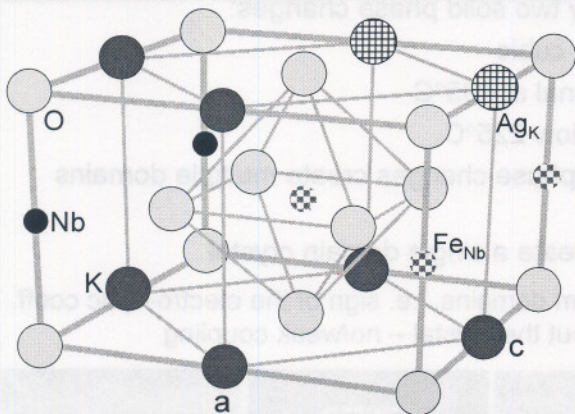


Fe

Ag adding to the melt



## KNbO<sub>3</sub> Lattice Structure



Fe with an O near & next near neighbor

Fe with a K next near neighbor

Fe with an Ag next near neighbor

Fe<sub>Nb</sub> and Ni<sub>Nb</sub> are interchangeable

Ag<sub>K</sub> and Rb<sub>K</sub> are interchangeable

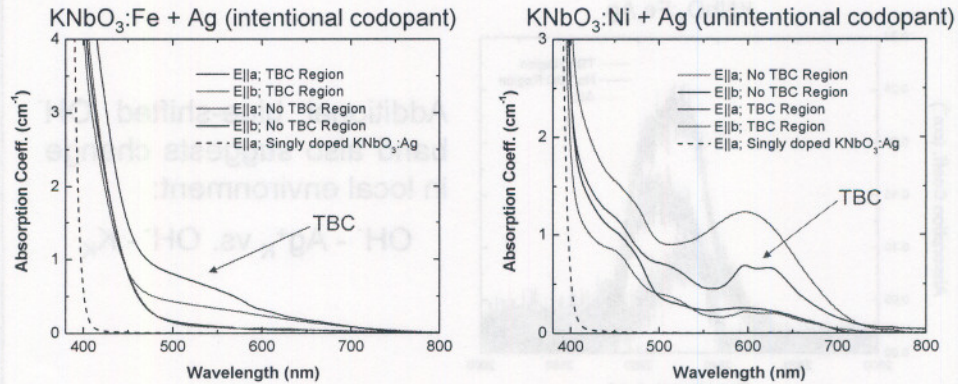
Element	+1	+2	+3	+4	+5
K	1.33				
Nb				0.74	0.69
Fe		0.74	0.64		
Ni		0.69			
Ag	1.26	0.89			

Schematic above does not reflect the distorted lattice

B. Zysset, et al., J. Opt. Soc. Am. B 9, (1992) 380, and K. G. Deshmukh et al., J. Phys. D: Appl. Phys. 4, (1971) 124.



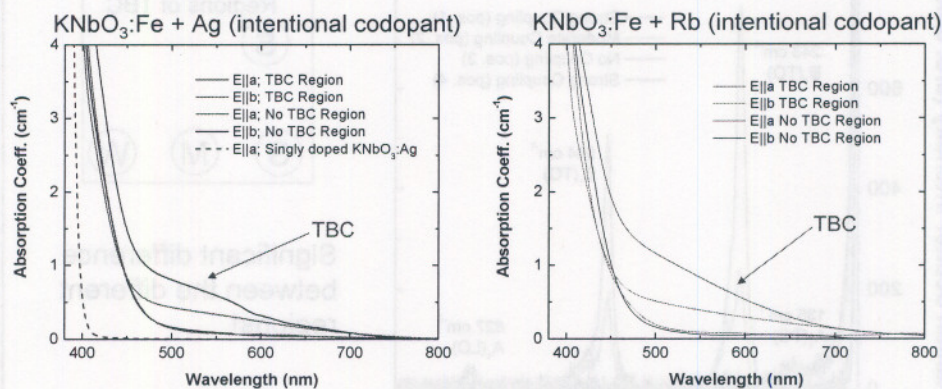
## Absorption Spectra (Visible Region)



In our geometry: TBC requires light polarized in the ac-plane



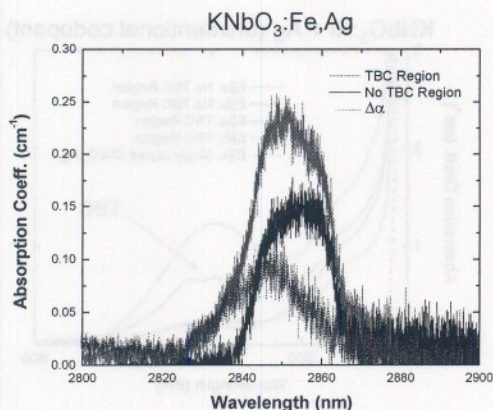
## Absorption Spectra (Visible Region)



In our geometry: TBC requires light polarized in the ac-plane



## Absorption Spectra (OH<sup>-</sup> Feature)



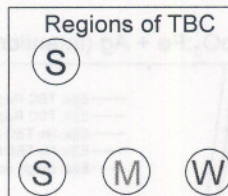
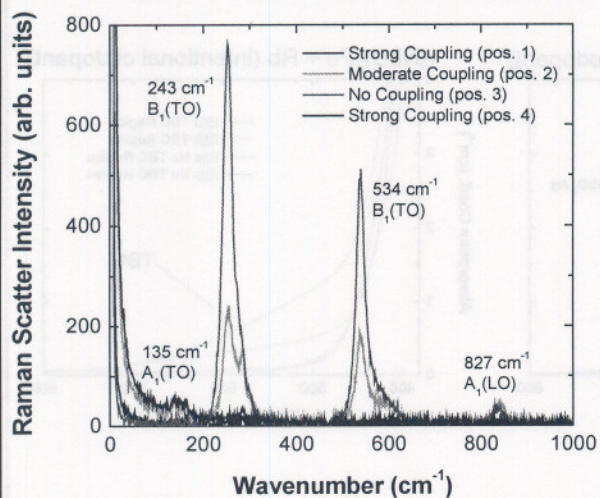
Additional blue-shifted OH<sup>-</sup> band also suggests change in local environment:



Light polarized in the ac-plane; E||a (TBC geometry)



## Raman Scatter (Asymmetric Modes)



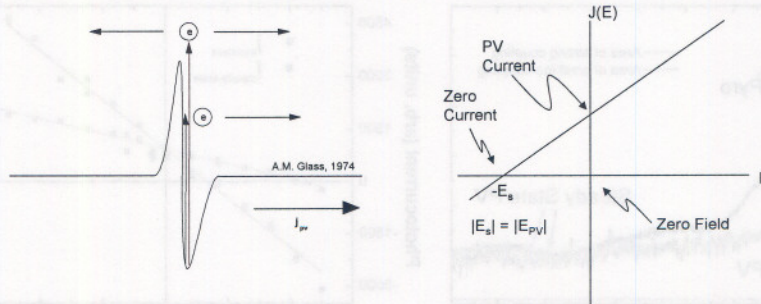
Significant difference between the different regions!

Asymmetric modes vanish in regions of strong coupling

<sup>1</sup>D. G. Bozinis and J. P. Hurrell, Phys. Rev. B **13**, 3109 (1976).



## Photovoltaic Effect

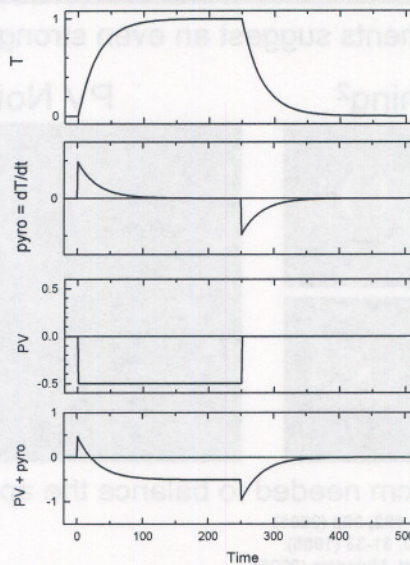


- PV field drives the electron in one directions (due to asym. potential)
- Applying an external E-field will oppose the current flow.
- At  $-E_s$  the photocurrent will equal zero, the effects of the PV and ext. E-field cancel out.

A. M. Glass, et al., Appl. Phys. Lett. 25, 233 (1974).

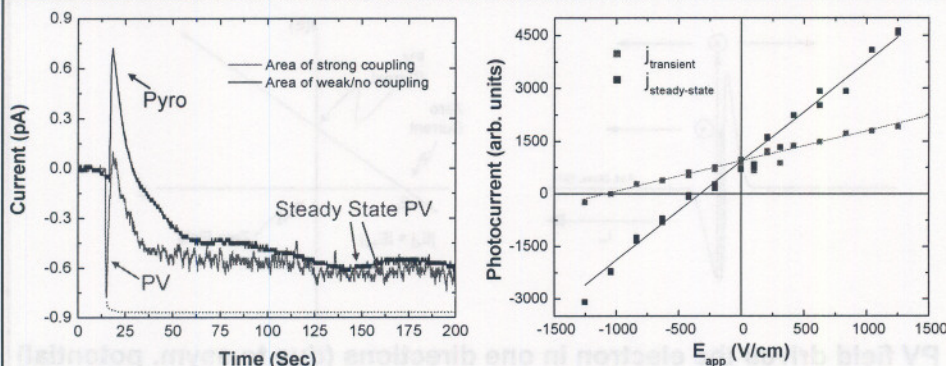


## Pyroelectric vs. Photovoltaic





## Photovoltaic and Pyroelectric Current Measurements



Explanation –

Initially, the PV current is strong, but:

- 1) is inhibited by pyroelectric current in strong-TBC region ( $\text{Fe}_{\text{Nb}} \rightarrow \text{Ag}_{\text{K}}$ )
- 2) is decreased as the space-charge field forms (i.e. large intensity gradient between front and rear of crystal)

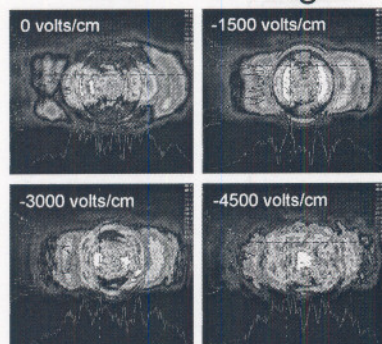


## Optical Photovoltaic Measurements<sup>1</sup>



Optical measurements suggest an even stronger PV field:

Beam Fanning<sup>2</sup>



PV Noise<sup>3,4</sup>



Estimate 15-20kV/cm needed to balance the apparent PV field

1. G. Cook, et al., Opt. Commun. **192**, 393 (2001).
2. S. Odoulov, et al., Opt. Lett. **10**, 31-33 (1985).
3. D. R. Evans, et al., in press Opt. Materials (2005).
4. D. R. Evans, et al., IEEE J. Quantum. Elec. **38**, 1661 (2002).



## Trap Density (Another Possibility)



- Theory<sup>1</sup> suggest PV fields (~20 kV/cm) alone, may not be enough to account for such large a photorefractive gain (TBC efficiency).
- The TBC efficiency (SCF) will also be strongly dependent on the trap density.
- An increase in trap density due to the incorporation of Ag would increase the space-charge field.

Steady-state the space-charge field:

$$E_{sc}(z) = \frac{-(E_0 + iE_d + E_{pv})m(z)}{1 + \frac{E_d}{E_q} - i\left(\frac{E_0}{E_q} + \frac{N_a E_{pv}}{N_d E_q}\right)}$$

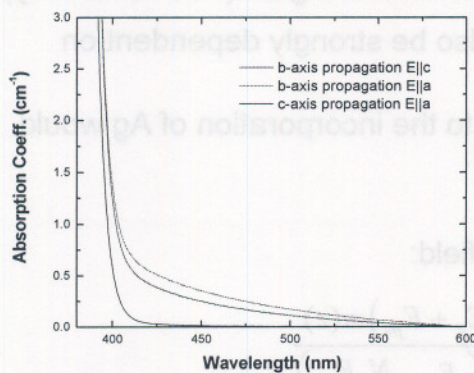
1. G. Cook, et al., Opt. Commun. **192**, 393 (2001).



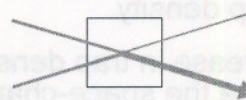
## Two-Beam Coupling Results



## Co-directional TBC in $\text{KNbO}_3:\text{Ag}$



Co-propagate along b,  $k||c$ ,  $E \perp a$



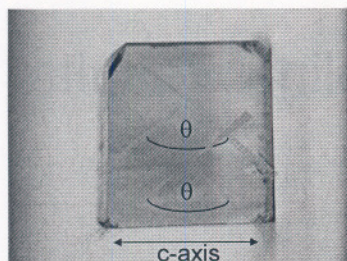
$$\Delta OD = 0.08$$

$$I_{\text{pump}} = I_{\text{signal}}$$

Hole Conductivity



## $\text{KNbO}_3:\text{Fe}$ (Ag diffused in during poling)



Unperturbed Fe region –  
Hole conductivity slow  
Small gain

Perturbed Fe region –  
Electron conductivity fast  
Large gain

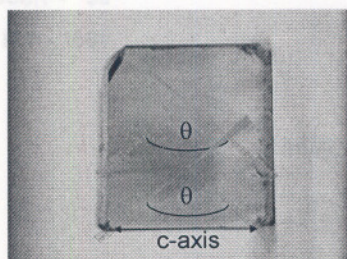
$$\Delta OD_{\text{Fe}} = 0.15$$

$$\Delta OD_{\text{Fe}'} = 0.35$$

i.e.  $\Gamma$  direction changes



## KNbO<sub>3</sub>:Fe (Ag diffused in during poling)



Perturbed Fe region –  
Electron conductivity fast  
Large gain

Unperturbed Fe region –  
Hole conductivity slow  
Small gain

$$\Delta OD_{Fe} = 0.15$$

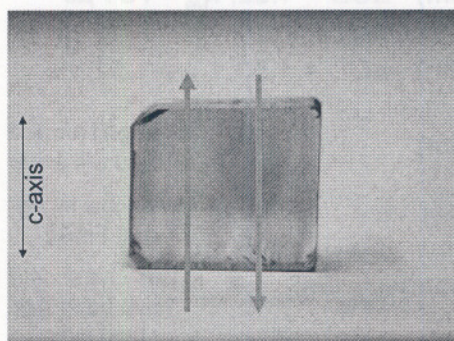
i.e.  $\Gamma$  direction changes

$$\Delta OD_{Fe'} = 0.35$$

$$\theta = 20^\circ$$



## KNbO<sub>3</sub>:Fe (Ag diffused in during poling)



Unperturbed Fe region –  
hole conductivity

Perturbed Fe region –  
electron conductivity

i.e.  $\Gamma$  direction changes  
No bipolar transport

$$\Delta OD_1 = 0.77, t_{1/e} = 28 \text{ ms}$$

$$20^\circ - 1.536 \mu\text{m}$$

$$180^\circ - 121 \text{ nm}$$

$$\Delta OD_2 = 1.5, t_{1/e} = 392 \mu\text{s}$$

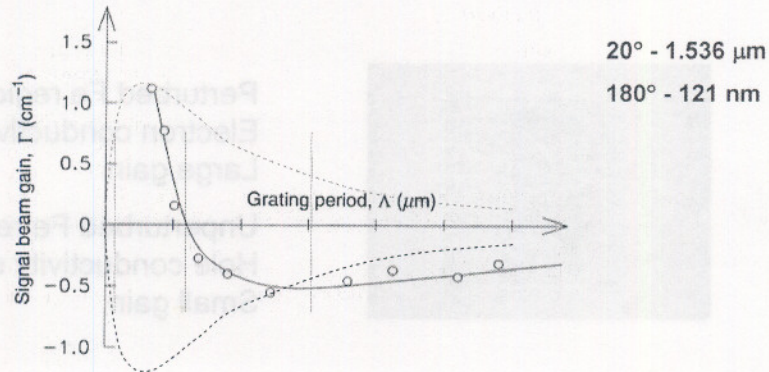
$$5 \text{ mW, } f/20$$



## Measurement for the "To-Do" List



Diffusion rates for holes and electrons are different.



Two-wave mixing gain as a function of grating period. Eg. anomalous  $\text{BaTiO}_3$  the cross over point at  $\Lambda = 0.6 \mu\text{m}$

\*L. Solymar, D. J. Webb and A. Grunnet-Jepsen, *The Physics and Applications of Photorefractive Materials*, Oxford Series in Imaging Science, vol. 11, Clarendon Press, Oxford, 1996.



## Performance of Doped $\text{KNbO}_3$



- $\text{KNbO}_3:\text{Fe,Ag}$  (1000/10000 ppm)  $\Delta\text{OD} = 1.52$ ;  $t_{1/e} = 784 \mu\text{s}$
- $\text{KNbO}_3:\text{Fe,Rb}$  (1000/10000 ppm)  $\Delta\text{OD} = 1.53$ ;  $t_{1/e} = 1.52 \text{ ms}$
- $\text{KNbO}_3:\text{Fe,Au}$  (1000/10000 ppm) X We don't know if Fe,Au will work
- $\text{KNbO}_3:\text{Ni,Ag}$  (1000/10000 ppm) X We know Ni,Ag and Fe,Ag
- $\text{KNbO}_3:\text{Fe,Ag}$  (1000/100000 ppm) X This one should have been the best ever

We should retry  $\text{KNbO}_3:\text{Fe,Ag}$  (1000/100000 ppm)  
and  $\text{KNbO}_3:\text{Fe,Au}$  (1000/10000 ppm)



## Mysteries?



Doping  $\text{KNbO}_3$  with:

Ag – hole conductivity

Fe – hole conductivity,

but...

Fe,Ag (perturbed Fe) – electron conductivity?

In  $\text{KNbO}_3$ :Ag – what is the acceptor?

Same question for  $\text{KNbO}_3$ :Fe and Fe' –

is it  $\text{Fe}^{3+}$  or some other species?



## Summary



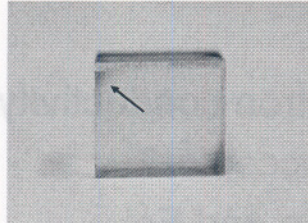
- Darker regions (perturbed Fe –  $\text{Fe}_{\text{Nb}}$  near a  $\text{Ag}_{\text{K}}$ ) in the crystal exhibit strong contra-dir.-TBC.
- There is a similar affect for interchanging  $\text{Ni}_{\text{Nb}}$  for  $\text{Fe}_{\text{Nb}}$  and  $\text{Rb}_{\text{K}}$  for  $\text{Ag}_{\text{K}}$ .  $\text{Au}_{\text{K}}$  should work as well, but there's no evidence yet.
- The presence of Ag changes the local environment, perturbing the other impurities (i.e.  $\text{OH}^-$ ), and the phonon/Raman modes are strongly affected.
- Ag was then purposely used as a codopant  $\text{KNbO}_3$ :Fe,Ag and is responsible for:
  - a stronger space-charge field
  - an enhanced visible/ $\text{OH}^-$  absorption
  - a stronger PV field
  - the strong affect on the Raman scatter
  - a possible increase in trap density (undetermined)
- Codoping with Ag is better than Rb in terms of speed, there's no significant difference in  $\Delta\text{OD}$ .
- Singly doped Ag and unperturbed Fe are hole conducting, whereas perturbed Fe and is electron conducting.



## Ag Codoping Status (Where We Are at the Moment)

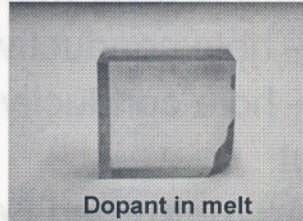


Started with a small mystery  
region in several crystals

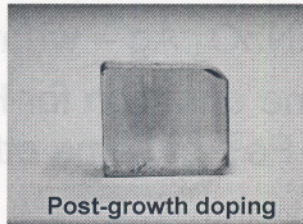


Assumed post-growth doping

Current status



Dopant in melt



Post-growth doping



## Summary



- Darker regions (perched  $\text{Fe} - \text{Fe}_{\text{OH}}$  near a  $\text{Ag}$ ) in the crystal exhibit strong contrast - TBC.
- There is a similar effect for interchanging  $\text{Fe}$  for  $\text{Fe}_{\text{OH}}$  and  $\text{Ag}$  for  $\text{Ag}_{\text{OH}}$ , but there's no evidence yet.
- The presence of  $\text{Ag}$  changes the local environment, perching the other impurities (i.e.  $\text{OH}^-$ ) and the phonon/Raman modes are strongly affected.
- $\text{Ag}$  was then purposely used as a codopant  $\text{KNO}_3\text{-Fe-Ag}$  and is responsible for:
  - a stronger space-charge field
  - an enhanced visible/IR absorption
  - a stronger PV field
  - the strong effect on the Raman scatter
  - a possible increase in trap density (undetermined)
- Codoping with  $\text{Ag}$  is better than  $\text{Fe}$  in terms of speed, there's no significant difference in  $\Delta\text{OD}$ .
- Singly doped  $\text{Ag}$  and unperturbed  $\text{Fe}$  are hole conducting, whereas unperturbed  $\text{Fe}$  and is electron conducting.